

SEASONAL VARIATIONS OF HYDROCARBONS IN THE WATER COLUMN
OF THE MAFLA LEASE AREA

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ABSTRACT

A series of 15 stations in the northeast Gulf of Mexico were occupied during summer, fall and winter 1975-76. Samples were collected and analyzed by gas chromatography for dissolved hydrocarbons and those associated with suspended particulate material. Average concentration of total resolved hydrocarbons was $0.4 \mu\text{g}/\ell$ dissolved and $0.3 \mu\text{g}/\ell$ particulate. Concentrations were higher near shore. Unresolved components were present in both dissolved and particulate phases, especially near the Mississippi River and Sound which may be the source of this material. Biogenic hydrocarbons, nC_{15} , nC_{17} , pristane and squalene in the particulate phase may be reflective of in situ biomass. A series of n-alkanes (nC_{21} to nC_{32}) in both dissolved and particulate phases persisted during all seasons. Squalene was the dominant molecule in the dissolved unsaturated/aromatic fraction at most stations, but was very low in concentration at the offshore stations in the fall. Total dissolved hydrocarbons correlates with dissolved organic carbon. Total particulate hydrocarbons did not correlate with particulate organic carbon or Chlorophyll a.

INTRODUCTION

The sale of oil and gas leases along the entire U. S. outer-continental shelf (OCS) and heightened public awareness of the potential harmful impact of petroleum-related activities, resulted in the initiation of environmental baseline and monitoring studies in the lease areas, under the sponsorship of the U. S. Department of Interior, Bureau of Land Management. The first

of these studies was the MAFLA (Mississippi-Alabama-Florida) program in the northeast Gulf of Mexico. During 1975-76, three sets of samples were collected from the water column in June-July 1975, September 1975 and January-February 1976. Dissolved hydrocarbons and those associated with suspended particulate matter were analyzed by my laboratory. This report represents our initial evaluation of the three data sets.

METHODS

Fifteen stations (Figure 1) in the northeast Gulf of Mexico were occupied during summer 1975, fall 1975 and winter 1976. At each station, 80 l of water was collected from a depth of 10 m with 30 l Niskin bottles. The Niskin bottles had been rinsed with methanol prior to use and were equipped with Teflon coated spring closures. The water was drained from the Niskin bottles through Teflon tubing into a precleaned stainless steel can of the type used to contain soft drinks at soda fountains. The o-ring gasket on each can was wrapped with Teflon film. The water was immediately poisoned with HgCl_2 and then filtered as soon as possible on board ship. Filtration was accomplished by pressurizing the storage can with prepurified nitrogen and forcing the water via Teflon tubing through a precombusted Whatman GF/F filter in a stainless steel Millipore filter holder and into a second stainless steel can. The filtrate was stored at ambient temperature until returned to the laboratory. The filters were wrapped in precombusted aluminum foil and frozen.

In the laboratory, the water was acidified to pH 2 with concentrated HCl and then extracted with doubly distilled chloroform or methylene chloride in two liter separatory funnels. Each extraction consists of 1500 ml of water and

3 x 50 ml of solvent. The total CHCl_3 (or CH_2Cl_2) extract was reduced to small volume in a rotary evaporator and then transferred quantitatively to a 25 ml round bottom flask. The remaining solvent was removed under a stream of prepurified nitrogen. After addition of 10 ml of 0.5 N KOH in methanol, the extract was saponified under reflux for at least four hours. Following addition of an equal volume of water, the non-saponifiable material was extracted into benzene (3 x 10 ml). The benzene was removed under nitrogen and the residue taken up in a small volume of hexane for column chromatography.

Filter pads were placed intact into an appropriately sized round bottom flask and covered with a 1:1 mixture of benzene and 0.5 N KOH in MeOH. After a four hour reflux the mixture was filtered through a precleaned glass fiber filter. Following addition of 25 ml of saline solution, the benzene layer was removed and the aqueous layer re-extracted with 3 x 25 ml of benzene. The benzene extracts were combined, reduced to dryness and taken up in hexane for column chromatography.

The non-saponifiable extracts in a small volume of hexane, were applied to a prewashed alumina overlaying silica gel column (1:3 v/v alumina to silica gel ratio, activity one) and eluted with two column volumes of hexane (aliphatic hydrocarbons) and two column volumes of benzene (unsaturated, aromatic fraction). The hexane fraction was reduced to small volume and the benzene fraction dried and taken up in a small volume of hexane for gas chromatography analysis.

Primary gas chromatographic analysis was done with 2.2 mm I.D. x 2 m

stainless steel columns packed with 4% FFAP on Gas Chrom Z, 80/100 mesh. Retention times were converted to retention indices utilizing known standards of n-alkanes. Peak areas were automatically integrated and converted to weight by applying GC response factors calculated from quantitative normal and isoprenoid alkanes and aromatics. These calculations as well as calculations of peak ratios, odd-even preference, wt. % composition and concentration were done by a computer program which produced both paper and magnetic tape output for submission to a central data bank.

Glassware was washed in detergent, soaked in acid, rinsed with distilled water and oven dried. solvent were doubly distilled. Periodic blanks were run and rejected if material with retention index greater than 1200 was present.

RESULTS - WATER

The gas chromatographically derived concentrations of the aliphatic and unsaturated/aromatic fractions are listed in Table 1 for all three seasons. In summer and fall the concentrations of the unsaturated/aromatic fraction generally exceeded that of the aliphatic fraction; this situation was reversed in the winter. The fall season had the lowest average hydrocarbon concentrations and the winter the highest.

Qualitatively, the dissolved hydrocarbons displayed regional differences during each sampling season. In the summer, two distinct regions were apparent (Figure 2a). Stations 1-7 displayed a unique bimodal envelope of unresolved components in the aliphatic fraction, with the maxima centered at C_{17} and C_{27} (Figure 2b). Stations 8-15 had a broad envelope with no

Table 1: Concentration of aliphatic(H), unsaturated/aromatic(B) and total (T) dissolved hydrocarbons.

Station	Summer			Fall			Winter		
	H	B	T	H	B	T	H	B	T
1	.11	1.01	1.12	.01	.15	.16	.69	.49	1.17
2	.14	.22	0.36	.05	.12	.17	.45	.18	.63
3	.13	.19	0.32	.08	.06	.14	.40	.06	.46
4	.39	.30	0.69	.04	.40	.45	.14	.10	.24
5	.14	.32	0.46	.02	.12	.13	1.08	.10	1.18
6	.08	.23	0.31	.02	.08	.10	.05	.23	.28
7	.25	.22	0.47	.10	.14	.24	.08	.04	.12
8	.05	.06	0.11	.02	.19	.21	.11	.03	.14
9	.17	.09	0.26	.11	.12	.23	.07	.35	.42
10	.25	.38	0.63	.06	.27	.32	.21	.07	.28
11	.10	.30	0.40	.09	.18	.27	.07	.08	.14
12	.17	.36	0.53	.12	.38	.50	.41	.09	.49
13	.09	.43	0.52	.06	.16	.22	.46	.15	.62
14	.13	.23	0.36	.02	.10	.12	1.14	.17	1.31
15	.06	.22	0.28	.16	.09	.25	.33	.03	.36
Avg	.15	.30	.45	.06	.17	.23	.38	.14	.54
	±.09	±.22	±.24	±.04	±.10	±.12	±.35	±.13	±.40

Table 2: Average concentrations of aliphatic (H) and unsaturated/aromatic (B) dissolved hydrocarbons.

Summer	H	B
Station 1-7 (bimodal envelope)	.18±.11	.36±.29
Station 8-15 (unimodal envelope)	.13±.07	.26±.13
Fall		
Station 1-8, 14 (no envelope)	.04±.03	.15±.10
Station 9-13, 15 (envelope)	.10±.04	.20±.11
Winter		
Station 1-5, 12-15 (envelope)	.56±.34	.15±.14
Station 6-11 (no envelope)	.10±.06	.13±.13

clear maximum (Figure 2c). Both groups of samples displayed a series of n-alkanes from C_{21} to C_{32} with the weight ratio of total odd carbon number to total even carbon number n-alkanes averaging 1.1 ± 0.1 . The unsaturated/aromatic fractions of both groups were similar (Figure 2d) and were generally dominated by a peak at $RI=3060$. Chromatography on a non-polar column (Figure 2e) confirmed the identity of this molecule as squalene. The concentration of squalene averaged $0.12 \pm 0.06 \mu g/l$. The concentrations of hydrocarbons in both fractions from the two groups were not significantly different (Table 2).

During the fall season, the concentration of dissolved hydrocarbons fell to about 50% of summer values (Table 1). This was true of both the aliphatic and unsaturated/aromatic fractions. Aliphatic fractions from stations 1-8 and 14 (Figure 3a) were characterized by a series of n-alkanes predominantly from C_{21} to C_{32} . The odd/even ratio for these fractions averaged 1.09 ± 0.10 . There was no detectable unresolved envelope at these stations. The remaining stations, 9-13 and 15, contained a definite envelope with a maximum near C_{27} (Figure 3c). The envelope was of lesser magnitude relative to the n-alkanes at stations 9 and 10. The series of from C_{21} to C_{32} was still present and had an average odd/even ratio of 1.04 ± 0.14 , excluding one value of 0.17. Samples which contained the envelope also had greater concentrations of resolved hydrocarbons in the aliphatic fraction, averaging $0.10 \pm 0.04 \mu g/l$ for those samples without an envelope (Table 2).

The unsaturated/aromatic fractions from the shoreward stations (Figure 3a) of each transect were similar to summer samples in that squalene

was the dominant molecule in this fraction (Figure 3d). The concentration of squalene at these stations averaged $0.06 \pm 0.03 \mu\text{g}/\ell$, excluding one value of **0.26** $\mu\text{g}/\ell$ at station 12. The offshore stations contained very little squalene (Figure 3e) averaging **0.00210.002** $\mu\text{g}/\ell$.

During the winter season, the presence or absence of an envelope in the aliphatic fraction divided the stations into coherent geographical units (Figure 4a). Stations 1-5 and 12-14 contained a large envelope with a maximum at C_{25} (Figure 4b) while stations 6-11 did not contain an envelope (Figure 4c). The concentration of resolved aliphatic hydrocarbons averaged 0.56 $\mu\text{g}/\ell$ at stations exhibiting the envelope and 0.10 $\mu\text{g}/\ell$ at stations without an envelope (Table 2). The odd/even ratio from both groups averaged 1.1. At all stations, a poorly resolved cluster of peaks with RI between 1600 and 1900 was present in relatively large amounts.

The concentrations of resolved hydrocarbons in the unsaturated/aromatic fraction did not depend on the presence or absence of an envelope in the aliphatic fraction, averaging 0.15 $\mu\text{g}/\ell$ and 0.13 $\mu\text{g}/\ell$ at stations with and without the aliphatic envelope. Squalene was present in the unsaturated/aromatic fraction at all samples with an average concentration at $0.04 \pm 0.03 \mu\text{g}/\ell$. Many of the samples also contained an unresolved envelope in this fraction, a feature not seen in previous seasons (Figure 2e, 4d).

RESULTS - PARTICULATE

The average concentration of resolved particulate hydrocarbons was 0.18 $\mu\text{g}/\ell$ in the summer, with most of the material being in the aliphatic fraction (Table 3). The dominant peak in the aliphatic fraction was nC_{15}

Table 3: Concentration of aliphatic (H), unsaturated/aromatic (B) and total (T) particulate hydrocarbons.

Station	Summer			Fall			Winter		
	H	B	T	H	B	T	H	B	T
1	.03	.04	.07	16.02*	1.36*	17.38*	.087	.027	.114
2	.66	.03	.69	.015	.002	.017	.050	.036	.086
3	.03	.01	.04	.011	0	.011	.323	.040	.363
4	.21	1.36*	1.57*	.113	.028	.141	.187	.022	.209
5	.06	.01	.07	.045	.006	.051	.151	.038	.189
6	.04	.03	.07	.050	.016	.066	.070	.024	.094
7	.18	.03	.21	.007	.004	.011	.058	.036	.094
8	.09	.05	.14	.144	.022	.167	.434	.193	.627
9	.07	.01	.08	.007	.003	.010	.073	.019	.092
10	.29	.01	.30	.014	.004	.018	.050	.020	.370
11	.09	.02	.11	.025	.010	.035	.080	.028	.108
12	.19	.21	.40	.095	.033	.128	3.341	.272	3.613
13	.13	.06	.19	.103	.052	.155	.391	.775	1.166
14	.09	.05	.14	.050	.007	.057	1.340	.046	1.386
15	.13	.01	.14	.088	.011	.099	.697	.220	.917
Avg	.14	.04	.18	.055	.014	.069	.49	.12	.62
	±.15	±.05	±.17	±.046	±.015	±.058	±.86	±.20	±.93

* omitted from average

with an average concentration of $.044 \pm .029 \mu\text{g}/\ell$. Pristane and $n\text{C}_{17}$ were present in all samples. An envelope in the aliphatic fractions was evident at stations 4 and 12-15 (Figure 5a). Its distribution maximum occurred around $n\text{C}_{23}$ (Figure 5b). A series of n-alkanes was superimposed on the envelope.

In the unsaturated/aromatic fraction, squalene was the dominant molecule with an average concentration of $0.016 \pm 0.014 \mu\text{g}/\ell$. A peak at RI 2350 was also prominent (Figure 5c).

In fall, the concentration of particulate hydrocarbons fell to about 40% of summertime values and averaged $0.069 \mu\text{g}/\ell$ (Table 3). The dominant feature was the presence or absence of the biogenic hydrocarbons $n\text{C}_{15}$, pristane, $n\text{C}_{17}$ and squalene (Figure 6a). In the aliphatic fractions, $n\text{C}_{15}$ was the dominant molecule and $n\text{C}_{17}$ and pristane were present at stations 1, 4, 5, 6, 8, 10-15 (Figure 6b). The concentration of $n\text{C}_{15}$ averaged $0.025 \pm 0.014 \mu\text{g}/\ell$ at these stations. At the remaining stations, 2, 3, 7 and 9, the biogenic hydrocarbons were essentially absent (Figure 6c) with the concentration of $n\text{C}_{15}$ being $0.001 \pm 0.001 \mu\text{g}/\ell$. Stations 1, 4 and 12-15 displayed envelopes in the aliphatic fraction, with station 1 having a very high concentration of both resolved and unresolved aliphatic hydrocarbons.

The unsaturated/aromatic fractions in the fall contained squalene and in general little else. The concentration of squalene averaged $.01 \pm .01 \mu\text{g}/\ell$ and $.003 \pm .004 \mu\text{g}/\ell$ at stations having and lacking, respectively, the aliphatic biogenic hydrocarbons.

The concentration of particulate hydrocarbons was greater during the

winter than the preceding seasons, averaging . 62 $\mu\text{g}/\ell$. However, there was a large range of .07 to 3.6 $\mu\text{g}/\ell$ (Table 3). Aliphatic fractions at all stations contained envelopes, with these being relatively large at stations 8 and 12-15 (Figure 7a). Biogenic hydrocarbons were essentially absent at all stations except 11 and 15 where nC_{15} averaged 0.02 $\mu\text{g}/\ell$. Envelopes were also present in the unsaturated/aromatic fraction at all stations being very large at 12-15. Squalene was very low or absent at all stations except 15 where its concentration was 0.03 $\mu\text{g}/\ell$.

DISCUSSION

The concentration of hydrocarbons in the water column of the MAFLA lease area compares well with the lower values reported in the literature for open ocean water. The overall average concentration was 0.4 $\mu\text{g}/\ell$ dissolved hydrocarbons, and 0.3 $\mu\text{g}/\ell$ particulate or 0.7 $\mu\text{g}/\ell$ total resolved hydrocarbons. Brown, et al. (1975) determined that total hydrocarbons in the open Atlantic and Pacific were about 1 $\mu\text{g}/\ell$ by an IR method. In the Mediterranean the concentration ranged from 2-8 $\mu\text{g}/\ell$ and near Bermuda the concentration was 3-6 $\mu\text{g}/\ell$. Levy (1971) reported values for total hydrocarbons of 2-13 $\mu\text{g}/\ell$ in the Atlantic off Halifax by a U_V-fluorescence method. Comparison of these results is made difficult because of the three different analytical methods used (G. C., IR, UVF) which are responsive to different portions of the hydrocarbons in the samples. Two reports of dissolved hydrocarbons by gravimetric analysis, which measures all hydrocarbons, indicate concentrations greater than reported above. Iliffe and Calder (1974) reported concentrations for aliphatic hydrocarbons of 12 $\mu\text{g}/\ell$ in the south-east Gulf of Mexico and Yucatan Straits and 47 $\mu\text{g}/\ell$ in the Florida Straits

while Barbier, et al. (1973) reported values of 43 and 95 $\mu\text{g}/\ell$ of total dissolved hydrocarbons from water collected at 50 m off the west coast of Africa. The gas chromatographically derived concentrations do not include contributions from the unresolved envelope when it is present. In those cases, total hydrocarbon may be a factor of ten greater than reported.

There is a general trend of higher total resolved hydrocarbon concentration near shore in both dissolved and particulate phases, although there are several exceptions to this trend.

The higher hydrocarbon concentrations near shore could be a result of direct terrestrial input or enhanced in situ production stimulated by terrestrially derived nutrients. The unresolved envelope components seem to have a terrestrial source, either Tampa Bay on Transect I, or the Mississippi River/Sound on Transect IV. These unresolved components could be the remnants of highly weathered crude oil from marine sources or waste oil from terrestrial sources. Both dissolved and particulate hydrocarbons contained a series of n-alkanes from nC_{21} to nC_{32} with an odd/even ratio of near unity. This feature might be the result of weathered petroleum residues, but could also be derived from marine phytoplankton (Clark and Blumer, 1967). This series of alkanes was present when the lower molecular weight biogenic alkanes were absent. If they are of recent biosynthetic origin, their stability in sea water must be greater than that of nC_{15} , nC_{17} and pristane.

The biogenic hydrocarbons nC_{15} , nC_{17} and pristane were dominant in the particulate aliphatic fraction and are probably the result of plankton collected on the filters. These hydrocarbons then should correlate with plankton biomass; however the remaining aliphatic and unsaturated/aromatic hydrocarbons in both dissolved and particulate phases are apparently not reflective

of in situ biomass. Thus total hydrocarbon should not correlate with biomass estimators, such as Chlorophyll a. No correlation was noted with Chlorophyll a values reported by Iverson (1976) on samples taken simultaneously with our hydrocarbon samples. This differs from the correlation between Chlorophyll a and total non-aromatic hydrocarbons reported by Zsolnay (1972) for waters off the west coast of Africa. However, the upwelling region off Africa was much richer in phytoplankton than the MAFLA region.

The total dissolved hydrocarbons did correlate with dissolved organic carbon analysis of samples collected simultaneously with hydrocarbon samples (Aller, 1976). The ratio of total dissolved hydrocarbons to dissolved organic carbon was $0.4 \pm 0.2 \mu\text{g}/\text{mg}$ in summer, $0.2 \pm 0.2 \mu\text{g}/\text{mg}$ in fall and $0.3 \pm 0.2 \mu\text{g}/\text{mg}$ in winter. The relative constancy of this ratio during each season indicates that the distribution of dissolved hydrocarbons and dissolved organic carbon are controlled by similar processes. No such relationship existed between particulate hydrocarbons and particulate organic carbon.

The high concentration of squalene in the water column is very interesting. A possible source for squalene is zooplankton (Calder, 1976). The total squalene in the average standing crop of zooplankton would be a few pg/ℓ , while the concentrations in the water column average several tens of ng/g . For zooplankton to be the source of squalene, it must have long term stability in the water column. Yet the absence of squalene at several stations in the fall indicates that squalene is subject to degradative or other loss mechanisms. The source and dynamics of squalene in sea water deserves further investigation.

CONCLUSIONS

1. Hydrocarbons in the water column of the MAFLA area exist at low levels comparable to open ocean values.
2. The presence of weathered petroleum in dissolved and particulate phases is indicated, but not proven, by the occurrence of unresolved envelopes and n-alkanes from nC_{21} to nC_{32} .
3. The unresolved envelope material may be derived from terrestrial sources.
4. Biogenic hydrocarbons in the particulate phase may be an indicator of in situ biomass, although there is not correlation of total hydrocarbon with Chlorophyll a.
5. There is a very high concentration of material with $RI=3060$ on FFAP and $RI=2810$ on SP-2100 in the water column. This material "is probably squalene.
6. Total dissolved hydrocarbon correlates well with dissolved organic carbon. There is no correlation between particulate hydrocarbons and particulate organic carbon.

D

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Figure 1. Station locations. Stations 1-3 are located on transect 1, stations 4-7 on transect 2, stations 8-11 on transect 3 and stations 12-15 on transect 4. Station numbering begins on the shoreward end of each transect.

B

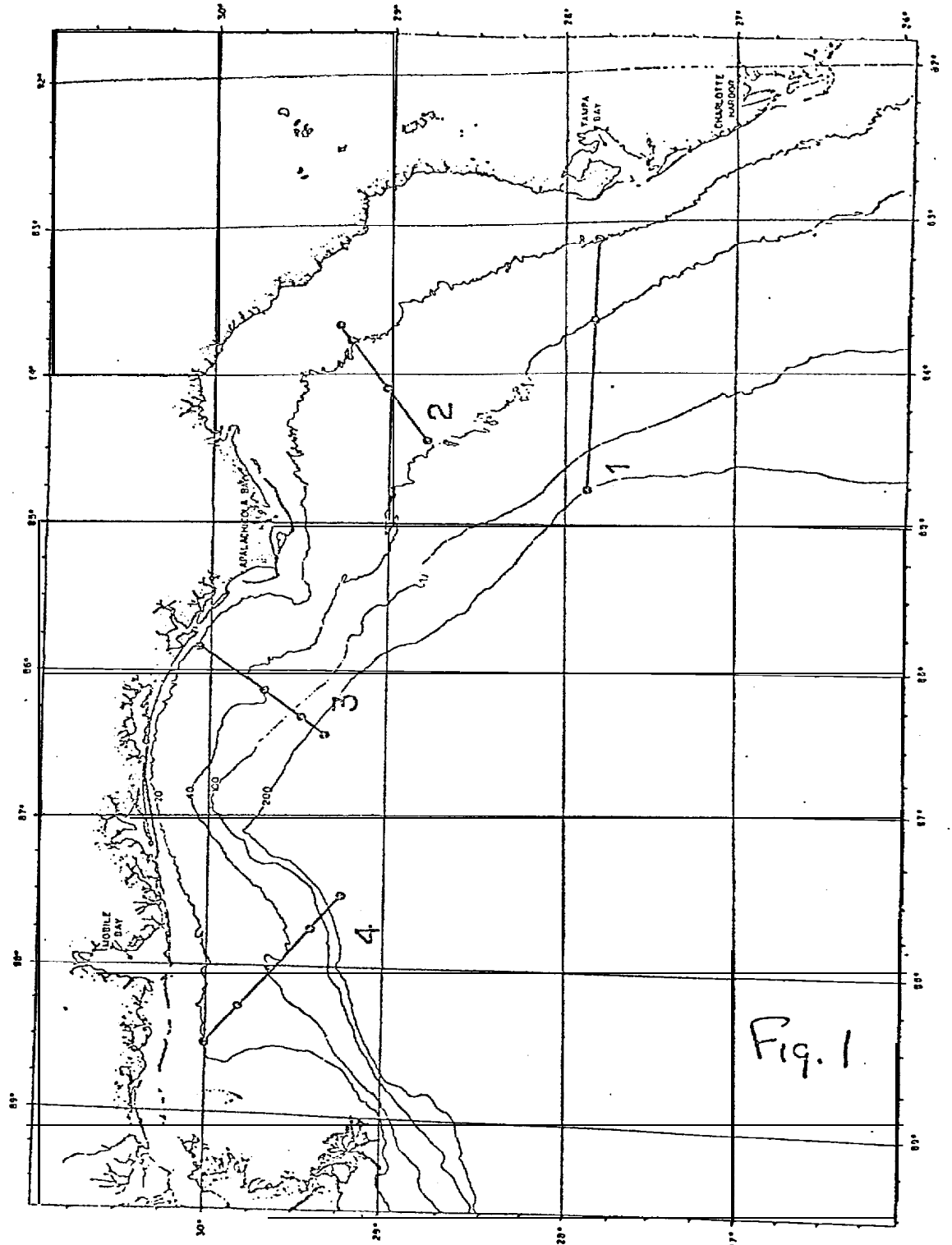


Figure 2a. Dissolved hydrocarbon distribution, summer 1975.

2b. Station 2, aliphatic fraction, dissolved hydrocarbons,
summer 1975.

2c. Station 12, aliphatic fraction, dissolved hydrocarbons,
summer 1975.

2d. Station 13, unsaturated/aromatic fraction, dissolved hydro-
carbons, summer 1975.

2e. Station 1, unsaturated/aromatic fraction, winter 1975.

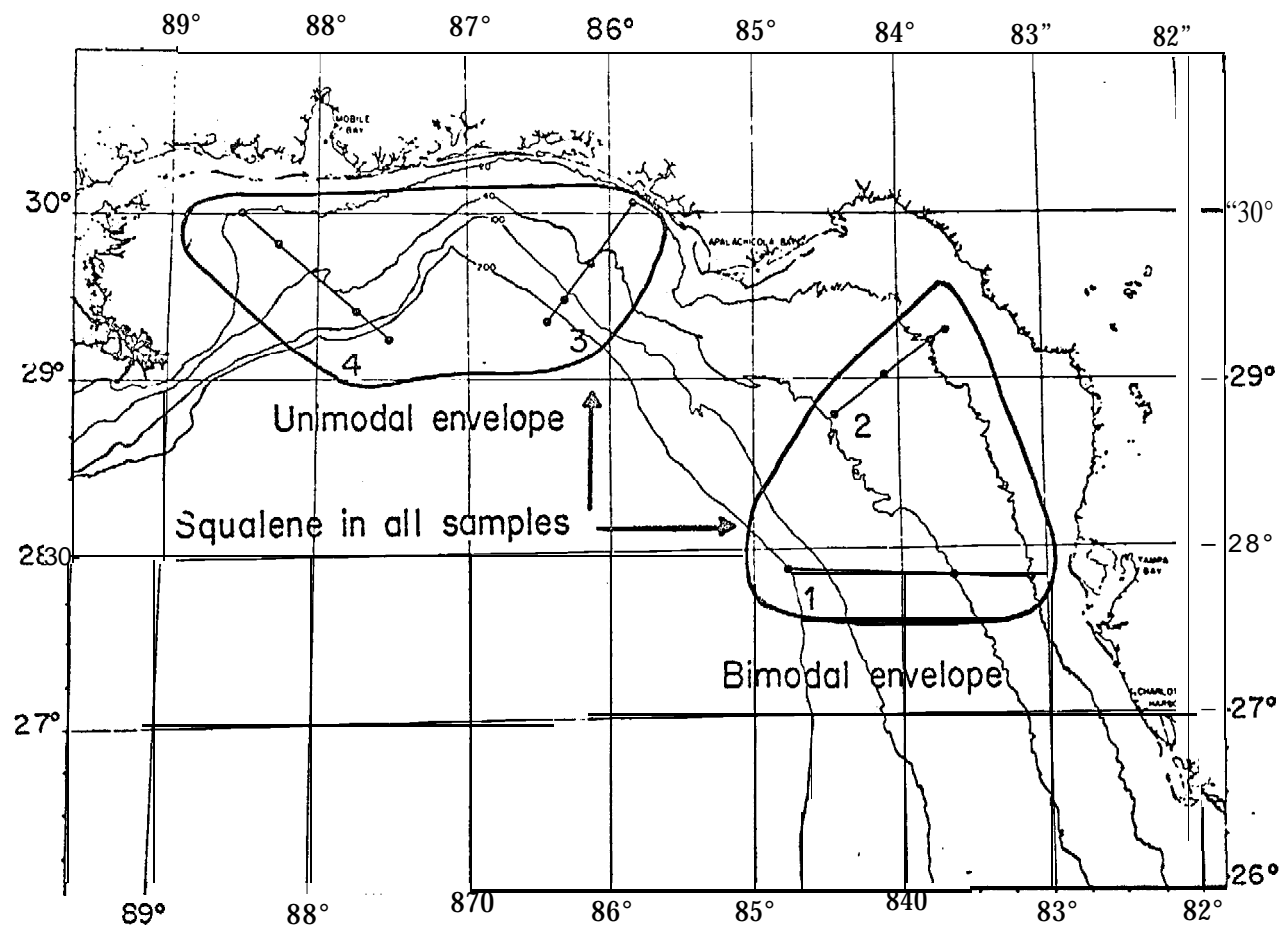


Figure 2a

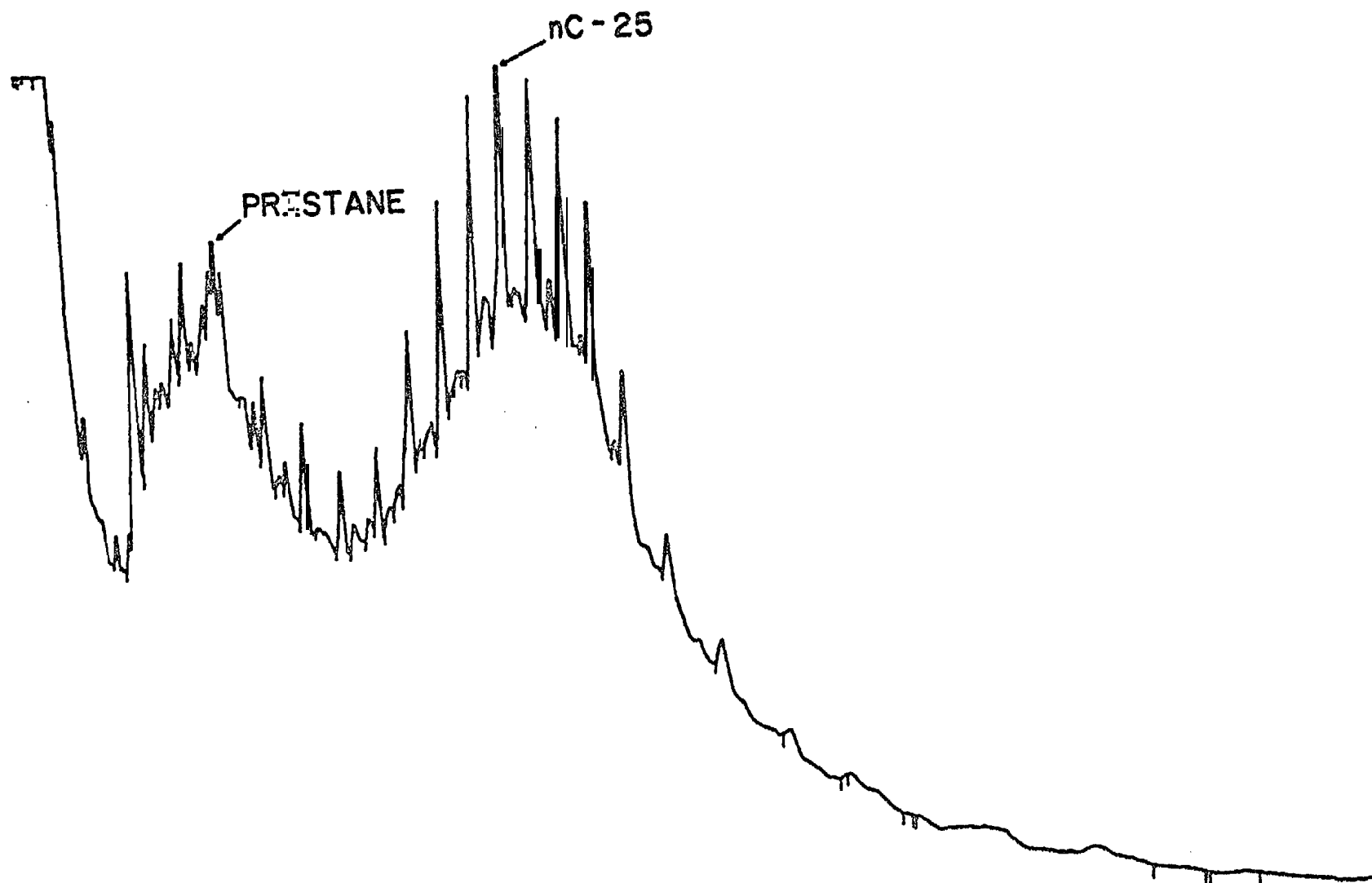


Figure 2b

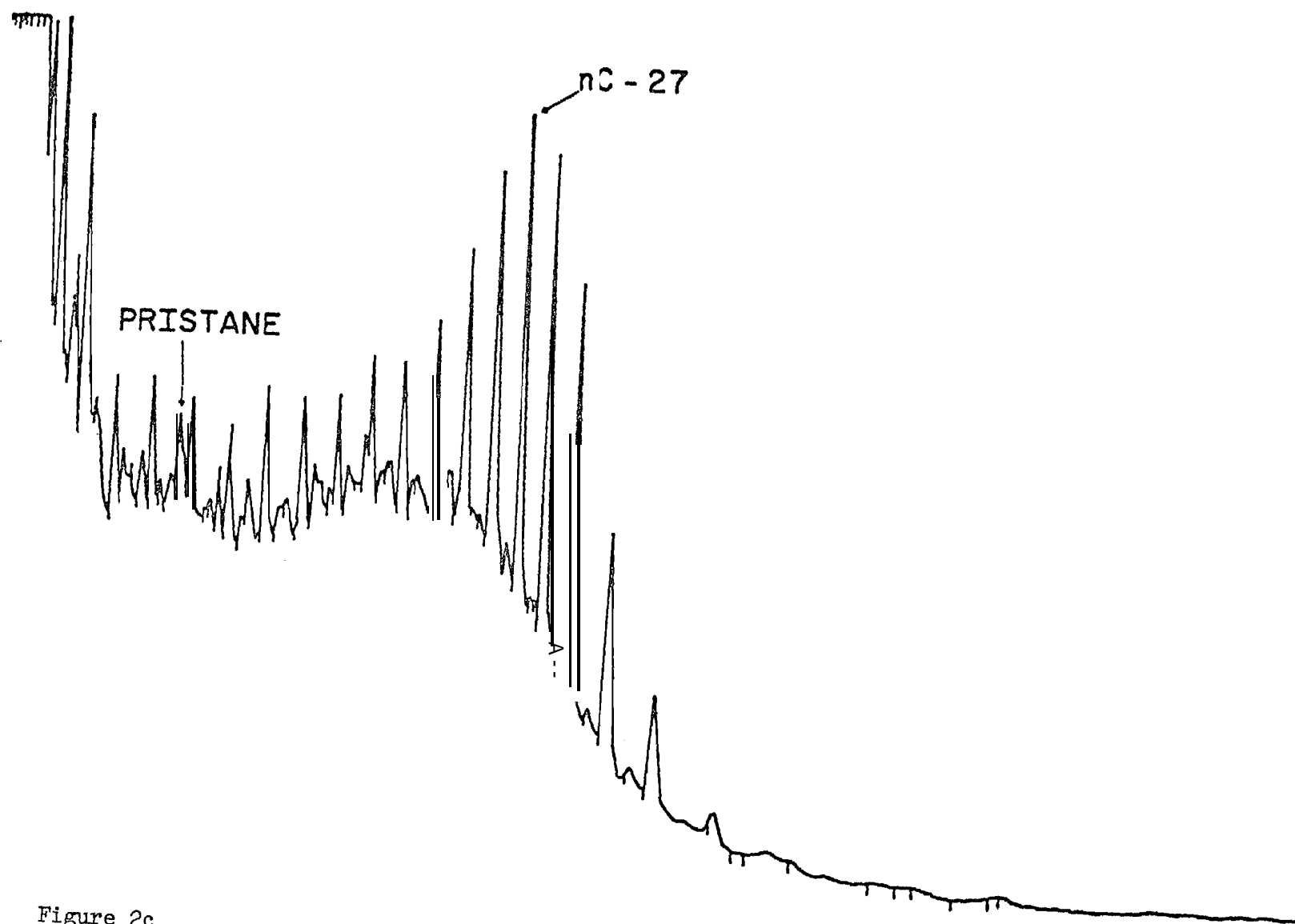


Figure 2c

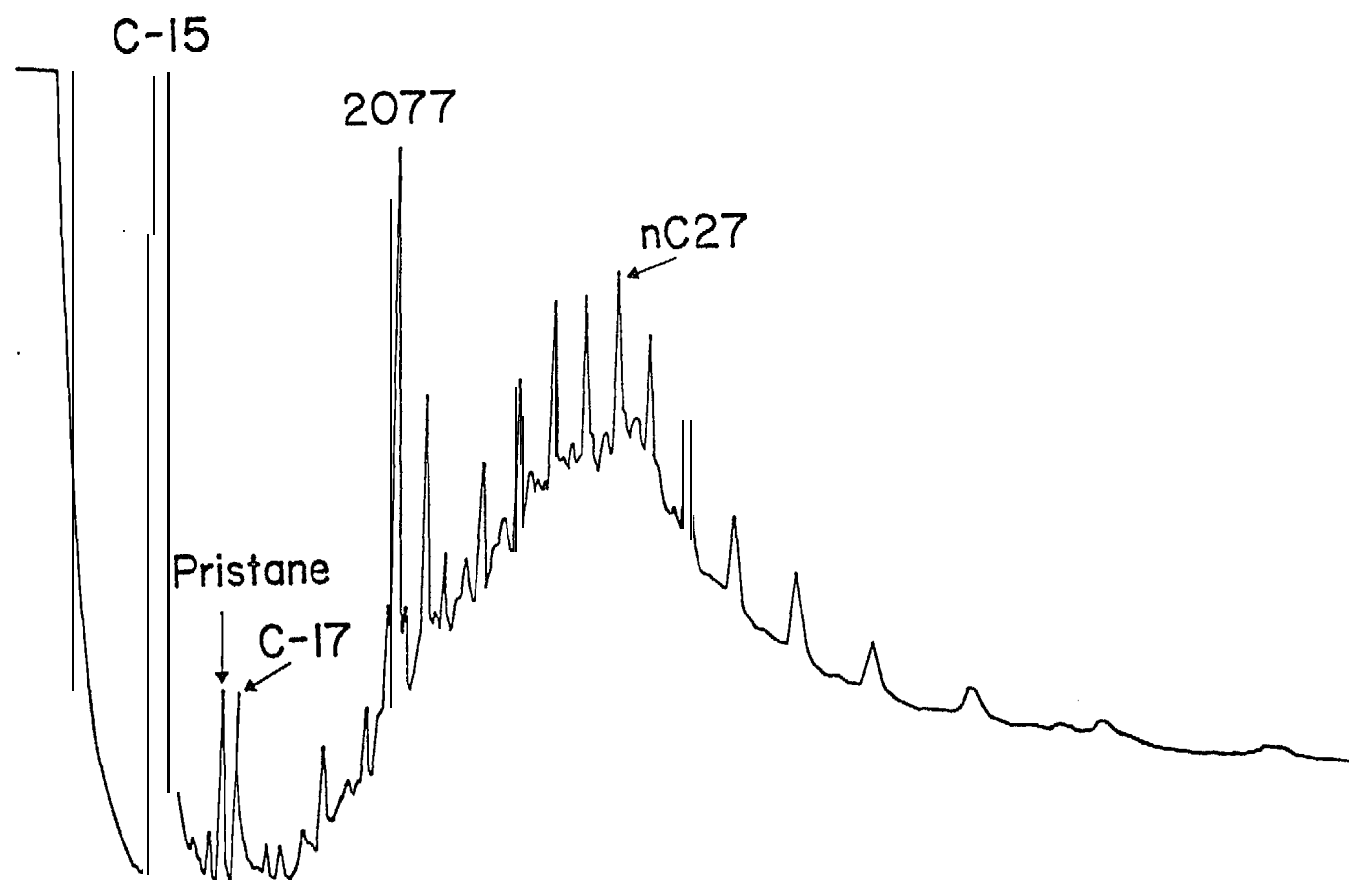


Figure 5b

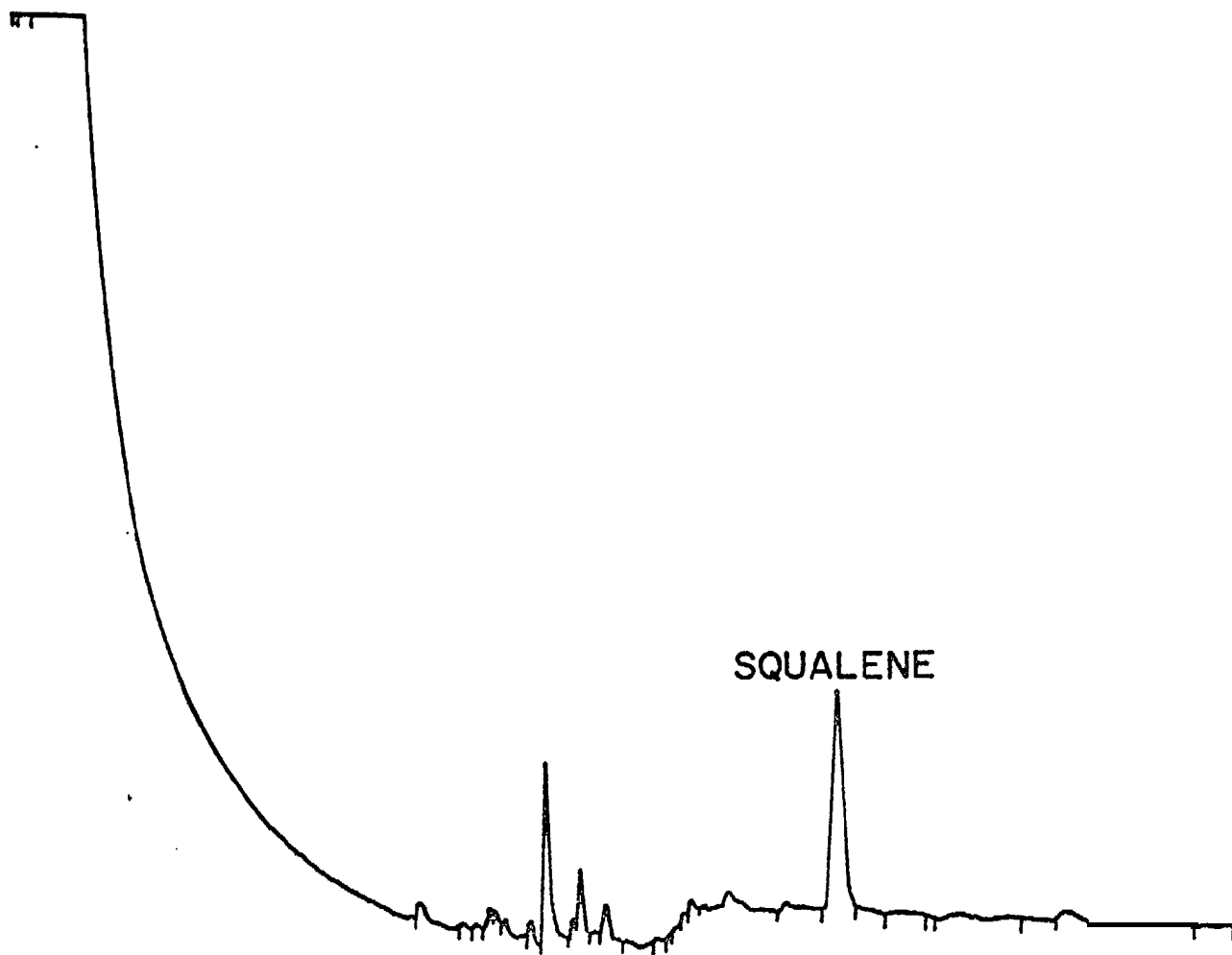


Figure 5c

B
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Figure 6a. Particulate hydrocarbon distribution, fall 1975.

6b. Station 4, aliphatic fraction, particulate hydrocarbons,
fall, 1975.

6c. Station 3, aliphatic fraction, particulate hydrocarbons,
fall 1975.

P

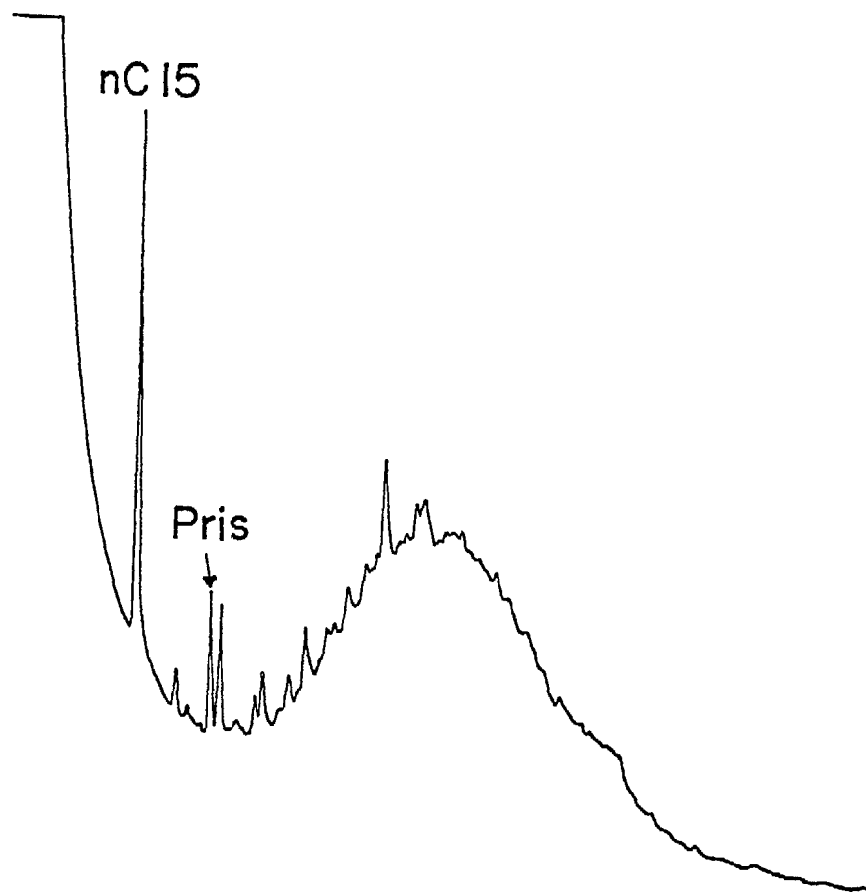


Figure 6b

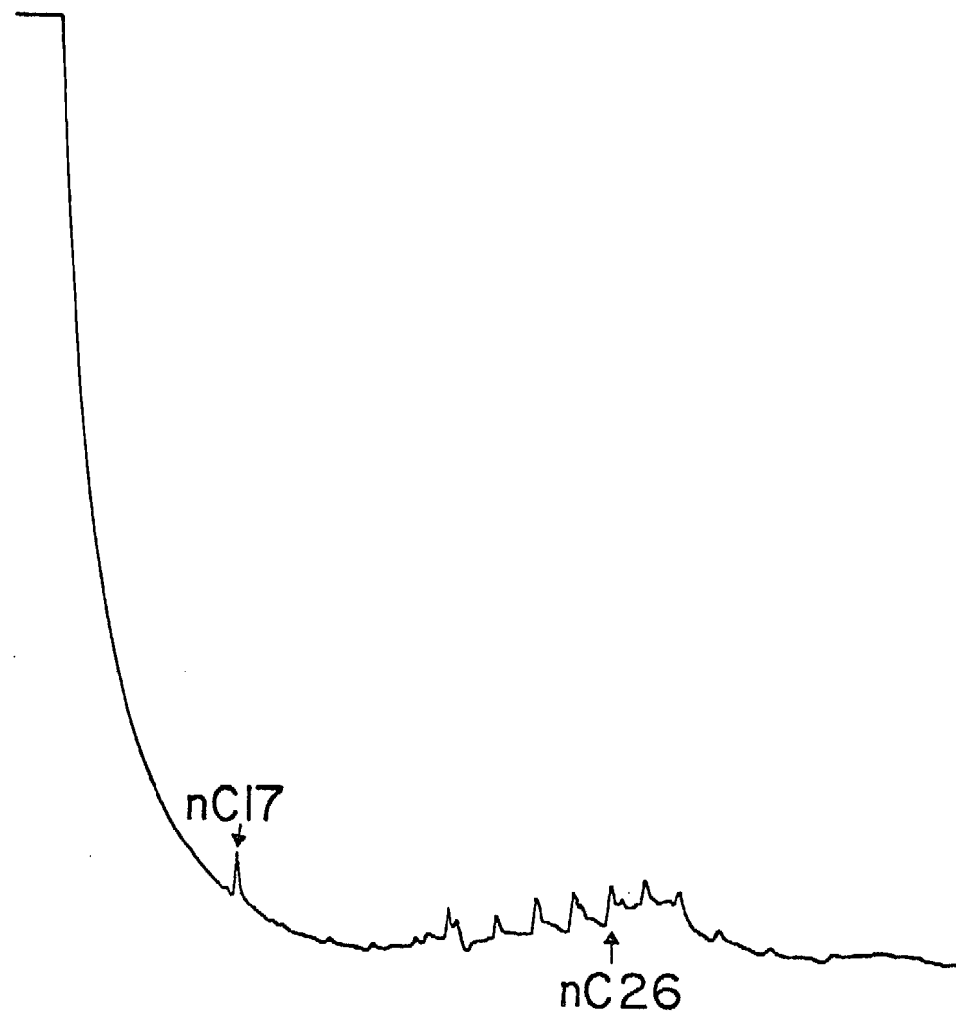
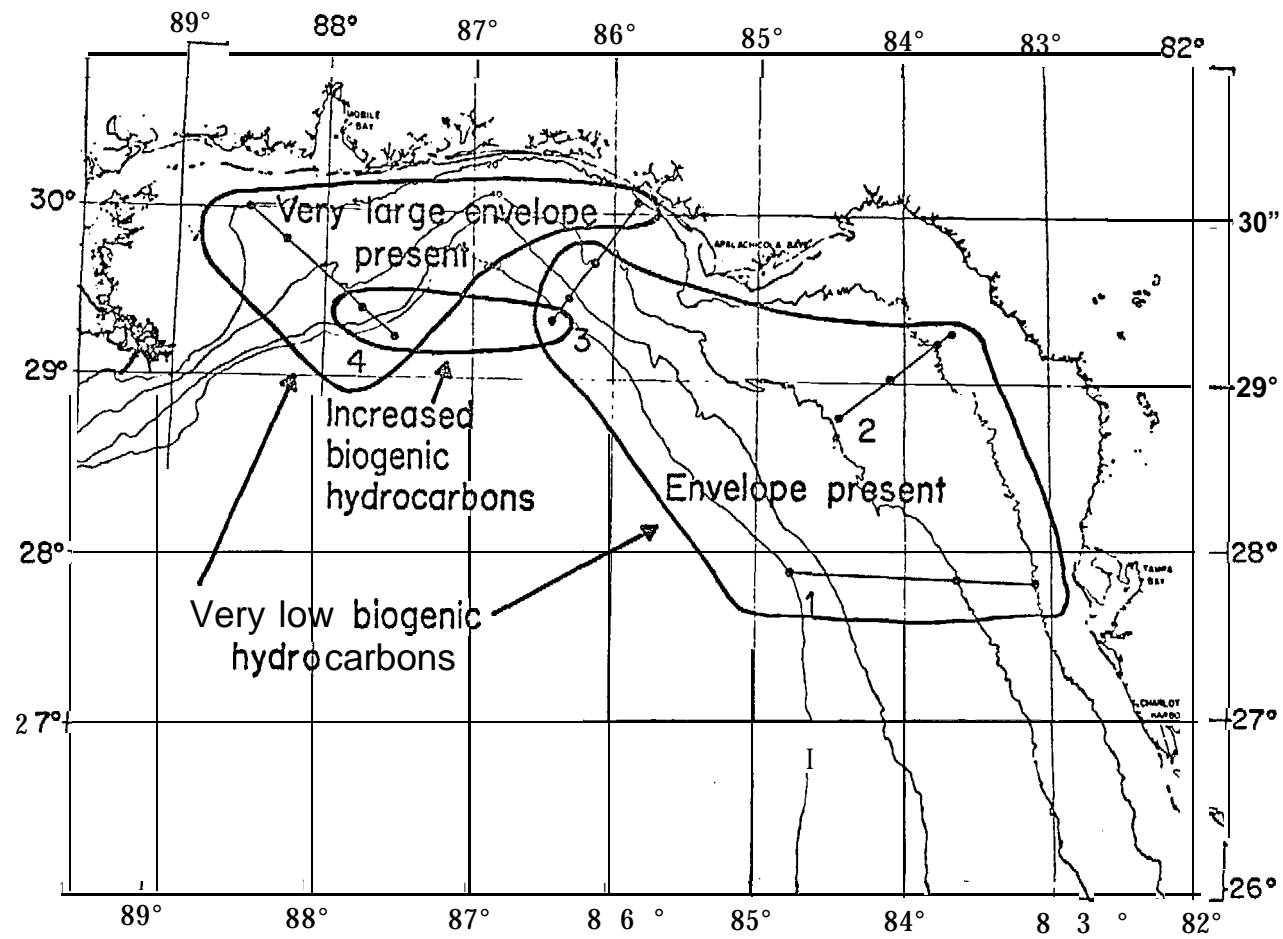


Figure 6c

Figure 7. Particulate hydrocarbon distribution, winter 1976.



• Figure 7